



Thin-film CoB catalyst templates for the hydrolysis of NaBH₄ solution for hydrogen generation

Palanichamy Krishnan^{*}, Suresh G. Advani, Ajay K. Prasad

Fuel Cell Research Laboratory, Department of Mechanical Engineering, University of Delaware, Newark, DE, USA

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ABSTRACT

Thin-film CoB alloy catalysts were prepared on Ni-foam substrates using electroless as well as electroplating techniques. Electroless plating was carried out using cobalt (II) sulfate as the source of Co²⁺, sodium succinate as the complexing agent, and dimethylamine borane as the source of boron as well as the reducing agent. Electroplating was carried out using cobalt (II) sulfate and cobalt (II) chloride as the sources of cobalt, and boric acid as the source of boron. The thin-film CoB/Ni-foam templates were characterized using ICP, XRD and SEM techniques. The normalized B content was in the range of 1.0–1.30 and 0.20–0.60 wt.% for electroless and electroplated templates, respectively. The B content is less than that required for stoichiometric alloy formation, which indicates the simultaneous deposition of the Co metal along with CoB alloy. An optimum condition of 0.100 M L^{−1} each of cobalt (II) sulfate heptahydrate Co(SO₄)·7H₂O, sodium succinate (Na₂C₄H₄O₄) and dimethylamine borane (CH₃)₂NHBH₃, at 60 °C with the pH value of 4–5 and a plating time of 1 h was identified for the preparation of the catalyst templates by electroless plating. Where as, 0.125 M L^{−1} each of cobalt (II) chloride hexahydrate (CoCl₂·6H₂O), Co(SO₄)·7H₂O, 0.125 M L^{−1} of boric acid at the current density range of 160–320 mA cm^{−2} and a temperature of 60 °C was identified as the optimum condition for the electroplating method. Maximum H₂ generation rates of 1.64 and 0.30 L min^{−1} g^{−1} of catalyst were obtained with electroless and electroplated thin-film CoB/Ni-foam templates, respectively. The suitability of the electroless plated CoB/Ni-foam catalyst template for extended duration of hydrogen generation from NaBH₄ was studied up to 60 h. Activation energies of 44.47 and 54.89 kJ mol^{−1} were calculated for electroless and electroplated CoB/Ni-foam catalyst templates, respectively.

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1. Introduction

Increasing global energy demand, limited fossil fuel reserves, and higher energy costs coupled with environmental concerns have motivated the search for various renewable sources of energy [1,2]. Hydrogen (H₂) is an attractive renewable energy carrier, abundantly present in nature, and has the potential to meet the increasing global energy demand [3]. Polymer electrolyte membrane (PEM) fuel cells that utilize H₂ as fuel are being developed as clean power generation devices for various uses ranging from portable power, residential use, and transportation applications [4,5]. However, widespread commercialization of PEM fuel cells is hindered due to challenges in setting up the H₂ supply infrastructure. Today, hydrogen is mainly produced by steam reforming of methane or electrolysis, and distributed in cylinders at pressures of approximately 350–700 bar. Apart from safety

concerns and high cost, high pressure H₂ storage suffers from poor gravimetric and volumetric efficiencies [6].

Considering the various issues with compressed H₂, the use of chemical hydrides to generate H₂ may offer a viable alternative. Chemical hydrides such as sodium borohydride (NaBH₄) which has 10.57 wt.% H₂ are very attractive [7–12]. Chemical hydrides undergo controlled hydrolysis in the presence of suitable catalysts to produce H₂ free from impurities. Catalysts reported initially for the hydrolysis of NaBH₄ were based on noble metals like Pt and Ru which are very expensive [7,8]. Subsequently, Wu et al. [9] reported the catalytic activity of cobalt boride (CoB) for the hydrolysis of NaBH₄. They prepared the catalyst by chemical reaction of aqueous NaBH₄ with CoCl₂ followed by heat treatment at 500 °C, and obtained a maximum H₂ generation rate of 2.97 L min^{−1} g^{−1} of catalyst. Following this initial work, many publications on the use of CoB catalysts for the hydrolysis of NaBH₄ have appeared in recent years. Jeong et al. [10] prepared the CoB catalyst by chemical reduction of CoCl₂ using NaBH₄ and reported the highest H₂ generation rate of 0.88 L min^{−1} g^{−1}. They also operated a passive air-breathing 2 W PEM fuel cell using the H₂

^{*} Corresponding author. Tel.: +1 302 831 8481; fax: +1 302 831 3619.
E-mail address: krishnan@udel.edu (P. Krishnan).

generated from NaBH_4 . In a subsequent publication [11], the same authors studied the effect of catalyst preparation conditions on H_2 generation and identified a $\text{NaBH}_4/\text{Co}^{2+}$ mole ratio of 1.5, and a catalyst heat treatment temperature of 250°C as the optimum parameters; they reported the maximum H_2 generation rate of $2.40\text{ L min}^{-1}\text{ g}^{-1}$. Tong et al. [12] prepared mesoporous CoB using triblock copolymer templates. The mesoporous CoB catalyst exhibited much higher catalytic activity than regular CoB. In all these studies, the CoB catalyst was prepared in powder form. The use of homogeneous powdered catalysts for H_2 generation has inherent disadvantages such as: (1) post-reaction separation and recycling of the catalyst from the viscous suspension is difficult; (2) the suspended particles tend to aggregate, especially at high concentrations; and (3) particulate suspensions are not easily applicable to continuous flow systems.

These difficulties could be circumvented by using catalysts in the form of thin films. Thin-film of catalyst coated on substrates like Ni foam, hereafter referred as catalyst templates are highly suitable for hydrogen-on-demand systems for the following reasons: the H_2 generation is initiated by simply inserting the thin-film catalyst template into the NaBH_4 solution, and the generation rate can be easily controlled by adjusting the contact area between the catalyst template and the NaBH_4 solution. Similarly, H_2 generation can be stopped by simply retracting the catalyst template from the solution. Therefore, the design of the H_2 generator could be simplified since a dedicated catalyst separation unit is not required. Furthermore, the thin-film catalyst templates could be continuously re-used thereby reducing the overall cost of the H_2 generation system. In a recent publication, Patel et al. [13] have reported the application of thin-film Co-B catalysts for H_2 generation from NaBH_4 . They prepared the thin-film CoB catalyst on glass substrates using pulsed laser deposition. Laser deposition is a complex and expensive procedure; moreover, the surface area of the catalyst is limited as it must conform to the two-dimensional planar surface of the template. Chemically bonded, durable thin-film Co-B catalysts could be prepared by employing electroless as well as electroplating techniques. Although several papers discuss the preparation of NiB [14], NiCoB [15] and FeCoB [16] alloy catalysts by electroless as well as electroplating techniques, the literature on the preparation of thin-film CoB alloys by these techniques as well as their application to NaBH_4 hydrolysis is very limited. Saito et al. [17] reported the preparation of a thin-film CoB alloy on a steel substrate using the electroless plating technique. The surface area of the plated CoB catalyst could be increased by employing high surface area templates such as metal foams. Lee et al. [18] impregnated a Ni-foam substrate with CoCl_2 and chemically reduced it with NaBH_4 to form CoB inside the Ni-foam structure. The process was repeated multiple times to obtain a coating of the desired thickness. Recently, Dai et al. [19] prepared thin films of Co_2B catalyst on Ni-foam substrates by following the same procedure as Lee et al. [18]. In both of these studies, the coating process had to be repeated multiple times to achieve the desired coating thickness which is laborious and time consuming. The aim of the current work is to prepare durable CoB alloy catalyst films on Ni-foam substrates using conventional electroless as well as electroplating techniques (pH range between 4 and 6). The H_2 generation activity of these catalysts, and their suitability for repetitive use as well as for extended operation is investigated.

2. Experimental details

2.1. Materials

Nickel foam (INCOFOAM^T) from Inco special products was used as the template for coating the CoB alloy catalyst. Boric acid

(H_3BO_3 , 99.0 wt.%), cobalt (II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 99.0 wt.%), cobalt (II) sulfate heptahydrate ($\text{Co}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$, 99.0 wt.%), dimethylamine borane ($(\text{CH}_3)_2\text{NHBH}_3$, DMB 99.0 wt.%), sodium succinate ($\text{Na}_2\text{C}_4\text{H}_4\text{O}_4$, 99.0 wt.%) from Across Organics, acetone (CH_3COCH_3 , 99.5 wt.%), sulfuric acid (H_2SO_4 , 99.5 wt.%), sodium hydroxide (NaOH , 99.50 wt.%), sodium tartrate dihydrate ($\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$, 99.0 wt.%) from Fischer Scientific Inc., sodium citrate dihydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$) from EMD Chemicals, USA, and sodium borohydride (NaBH_4 , 98.5 wt.% VENPURETM) from Rohm and Haas were used in this study. The chemicals were used as received without any further purification.

2.2. Preparation of thin-film CoB/Ni-foam templates by electroless and electroplating techniques

Nickel foam, 0.17 cm thick was cut into $2\text{ cm} \times 2\text{ cm}$ square specimens, washed with acetone followed by de-mineralized (DM) water and dried at 110°C . The specimens were weighed and activated in 10 wt.% H_2SO_4 for 10 min, washed with DM water and transferred to the electroless plating bath. The specimens were mounted inside the plating bath with a clamp. The plating bath was prepared by dissolving the respective bath components in DM water. Typical bath composition and plating conditions are given in Table 1. The pH of the bath was maintained between 4 and 5 by adding either 1.0 M NaOH or 1.0 M H_2SO_4 solution. For the electroplating process, a stainless steel specimen of same dimensions as the Ni-foam template was used as the anode. DC current was supplied from a regulated power supply and an ammeter was connected in series to monitor the current. After plating, the specimens were removed from the bath, washed to remove the adhering solution, and weighed to determine the quantity of the plated CoB alloy. The composition of the catalyst coated templates was determined by inductively coupled plasma (ICP) analysis.

2.3. Characterization of the catalysts by X-ray diffraction measurement

X-ray powder diffraction patterns were obtained at room temperature on a Rigaku MiniFlex powder diffractometer using Ni filtered $\text{Cu K}\alpha$ adiation. All of the runs included θ - θ scans ($2\theta_{\text{max}} = 90^\circ$) with intervals of 0.05° and a 1 s counting time. The data analysis was carried out using the JADE 6.5 software package.

2.4. SEM

The surface morphology as well as cross-sections of the Ni-foam substrate, and the catalyst coated templates were examined by scanning electron microscope (SEM), JSM-7400 from JOEL Ltd., Japan. For the surface morphology, a small section of the template was cut and fixed on to the SEM sample holder using double-sided tape. For the cross-sectional examination, a fresh cross-section was

Table 1

Bath composition and plating conditions for electroless plating of CoB thin-film alloy on Ni-foam templates

Chemicals	Concentration (M)
$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	0.10
$\text{Na}_2\text{C}_4\text{H}_4\text{O}_4 \cdot 6\text{H}_2\text{O}^a$	0.10
$(\text{CH}_3)_2\text{NHBH}_3$	0.10
Bath pH	4–5
Bath temperature ($^\circ\text{C}$)	60
Plating time (h)	1–4

^a 0.1 M $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$.

Table 2
Composition of electroless plated CoB/Ni-foam templates

Experimental condition	Composition (wt.%)		
	Ni	Co	B
1 h plating	41.63	57.75	0.61
2 h plating	37.22	61.99	0.77
4 h plating	33.93	65.21	0.85

cut using sharp scissors and examined; a thin layer of Au–Pd was sputtered before examination.

2.5. H_2 generation experiments

In a typical H_2 generation experiment, 25 ml of $NaBH_4$ solution was placed in a thermostated tubular glass vessel maintained at 25 °C. The template was immersed in the solution using a clamp. The generated H_2 was measured using a mass flow meter whose output was continuously recorded by a computer. Suitability of the catalyst templates for extended operation was studied in a 1000 ml capacity tubular reactor. About 700 ml of 10 wt.% $NaBH_4$ (5 wt.% NaOH) solution was placed in the reactor and the experiment was continued until all the $NaBH_4$ in the solution was hydrolyzed.

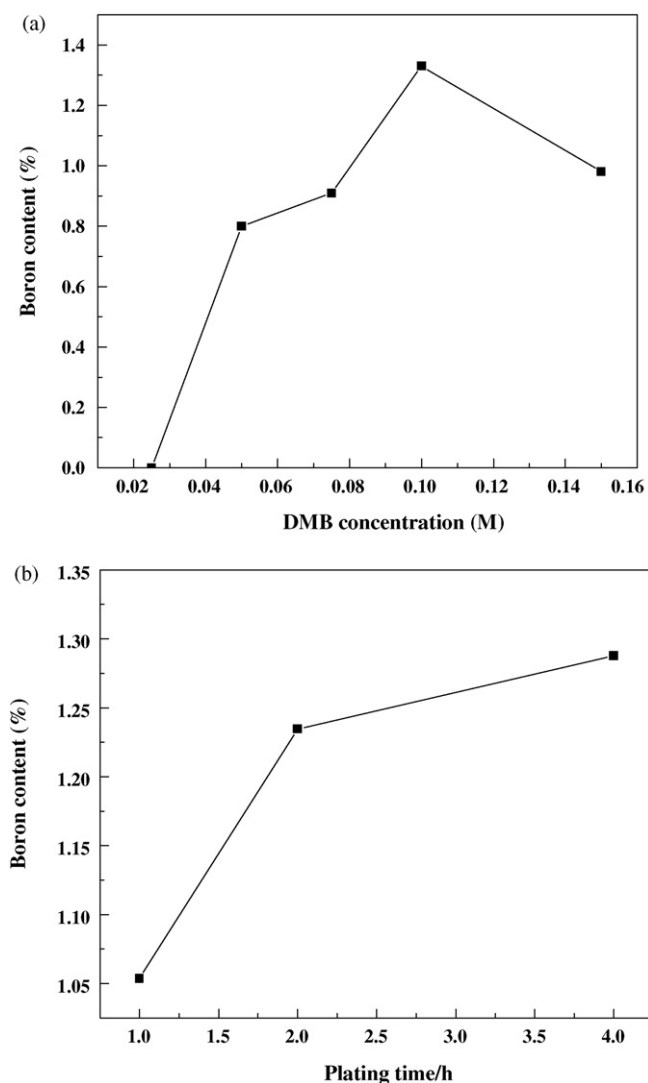


Fig. 1. Normalized wt.% of boron in the electroless plated samples. (a) For various concentrations of dimethyl amineborane (DMB), (b) with variation of plating time.

2.6. Activation energy calculation

The experimental set-up is the same one described in the earlier section for H_2 generation. A small piece of the catalyst template was cut and weighed to determine the weight of CoB catalyst present in the template. Then, the template was immersed in the $NaBH_4$ solution using a clamp. The H_2 generation vessel was assembled inside the water bath; temperature of the water bath was continuously increased. The rate of H_2 generation as well as temperature inside the vessel was continuously recorded. The rate of hydrogen generation at different temperatures was used to calculate the rate constant and plotted against $1/T$ to obtain the activation energy as described in Section 3.3.

3. Results and discussion

3.1. Electroless plating

Bath composition and plating conditions used for plating the Co–B alloy catalyst film on Ni-foam substrates are listed in Table 1. Three complexing agents, namely sodium succinate, sodium citrate, and sodium tartrate were used to maintain the Co^{2+} in complex form. Stability of the bath was poor when sodium tartrate was used as the complexing agent. Stability as well as throwing power were good with sodium succinate and hence it was used as

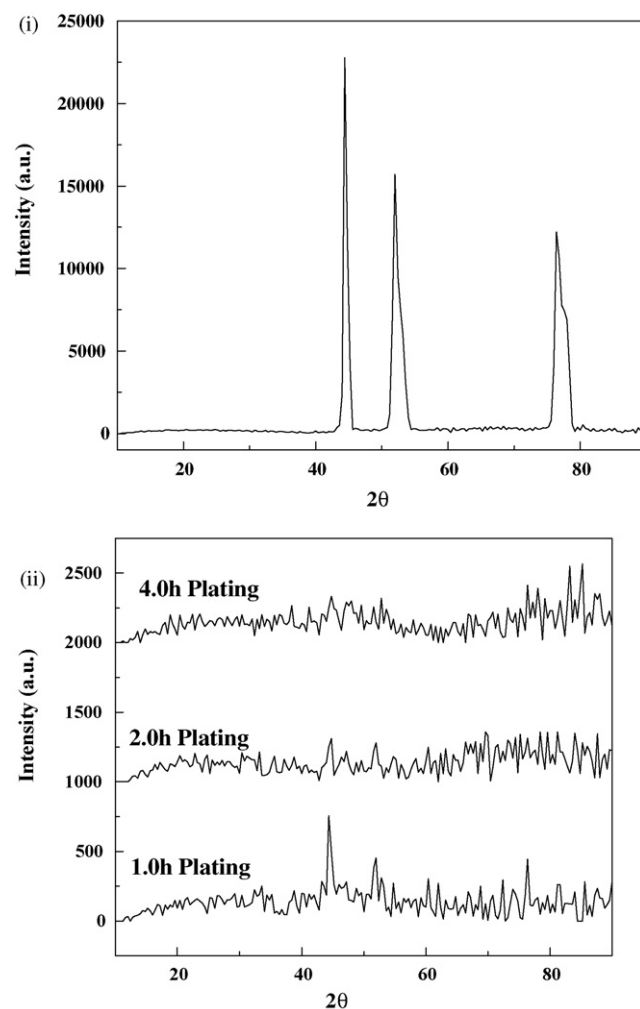


Fig. 2. X-ray diffraction: (i) Ni-foam template; (ii) electroless plated CoB/Ni-foam templates.

the complexing agent throughout this study. The catalyst coated templates were dissolved in nitric acid (HNO_3) and analyzed by ICP to determine the weight percentages (wt.%) of Ni, Co and B. Typical compositions of the templates after different plating times are given in Table 2. The wt.% of Co and B increased with plating time. However, the wt.% of B is less than that required for stoichiometric CoB compounds like CoB, Co_2B or Co_3B [20]. Low wt.% of B in the deposits indicates that the Co metal is simultaneously getting deposited along with CoB alloy. Normalized wt.% of B in the deposited CoB alloy for various concentration of DMB as well as plating time are plotted in Fig. 1(i) and (ii). The B content in the deposit increased with DMB concentration and reached a maximum value of 1.33% for 0.100 M concentration of DMB in the bath. The B content decreased with further increase in DMB concentration; this could be due to increased rate of Co metal deposition. Even then, wt.% of B in the deposits prepared in this study is comparable to that reported by Saito et al. [17] for the electroless coated CoB alloy deposits. It has also been reported [17] that the catalytic activity for the oxidation of DMB and the tendency for boride formation was less in the CoB system; this could be the reason for the smaller B content in the electroless plated deposits.

X-ray diffraction patterns of the Ni-foam substrate as well as that of the Co-B catalyst coated templates at different plating times are given in Fig. 2. The Ni-foam substrate shows three characteristic diffraction peaks for nickel ($2\theta = 44.5^\circ$ (1 1 1), 51.8° (2 0 0) and 76.4° (2 2 0)) indicating the face centered cubic phase of nickel [21]. However, the diffraction peaks of Ni are masked in the catalyst coated templates (Fig. 2ii). The diffraction peaks of Ni are weak in the 1 h plated sample and almost absent in the 4 h plated sample. Absence of diffraction peaks indicates the amorphous nature of the coating; CoB is amorphous and does not show strong peaks in X-ray diffraction [9]. Since the coating obtained in the present study is a mixture of CoB and Co, the absence of diffraction peaks indicates that the deposited Co is also amorphous in nature.

SEM micrographs of the surface of the Ni-foam substrate, and the surface as well as the cross-section of electroless plated templates are shown in Fig. 3. The SEM micrographs reveal excellent adherence of the catalyst coating on the Ni-foam substrate, which is highly desirable for the extended usage of these templates for H_2 generation. The cross-sectional view also confirms the intimate adherence as well as dense morphology of the coating. The thickness of the coating is around 10–15 μm which is higher than the wall thickness of the hollow foam substrate.

H_2 generation rates obtained using three templates with the plating times of 1, 2 and 4 h as well as the effect of NaBH_4 concentration on the rate of H_2 generation are presented in Fig. 4(a). The maximum H_2 generation rate of $1.46 \text{ L min}^{-1} \text{ g}^{-1}$ of the catalyst was obtained with the 1 h plated template. The maximum H_2 generation rate reduced with increased plating time and a maximum of $0.90 \text{ L min}^{-1} \text{ g}^{-1}$ was obtained with the 4 h plated template. The Ni-foam substrate has a cell size of 400–850 μm so with an increase in plating time, the thickness of the coating increases to such an extent that both the cell size as well as the active catalyst area are reduced. Both of these would reduce the rate of H_2 generation; reduction in cell size will impede mass transfer and increase in plating thickness will reduce the active catalyst area.

Since NaBH_4 based hydrogen generators are being developed for portable fuel cells, the use of highly concentrated NaBH_4 solution as the fuel will help to reduce the overall weight of the fuel cell power pack. However, the stability of NaBH_4 solution towards hydrolysis increases with NaBH_4 concentration due to enhanced alkalinity of the concentrated solution. Hence, it is very important to evaluate the effect of NaBH_4 concentration on the performance of the catalyst. We investigated the performance of the electroless plated catalyst templates in NaBH_4 solutions varying in concentration from 5 to 30 wt.% and the results are shown in Fig. 4(b). The H_2 generation rate was highest, i.e. $1.6 \text{ L min}^{-1} \text{ g}^{-1}$ with 5 wt.%

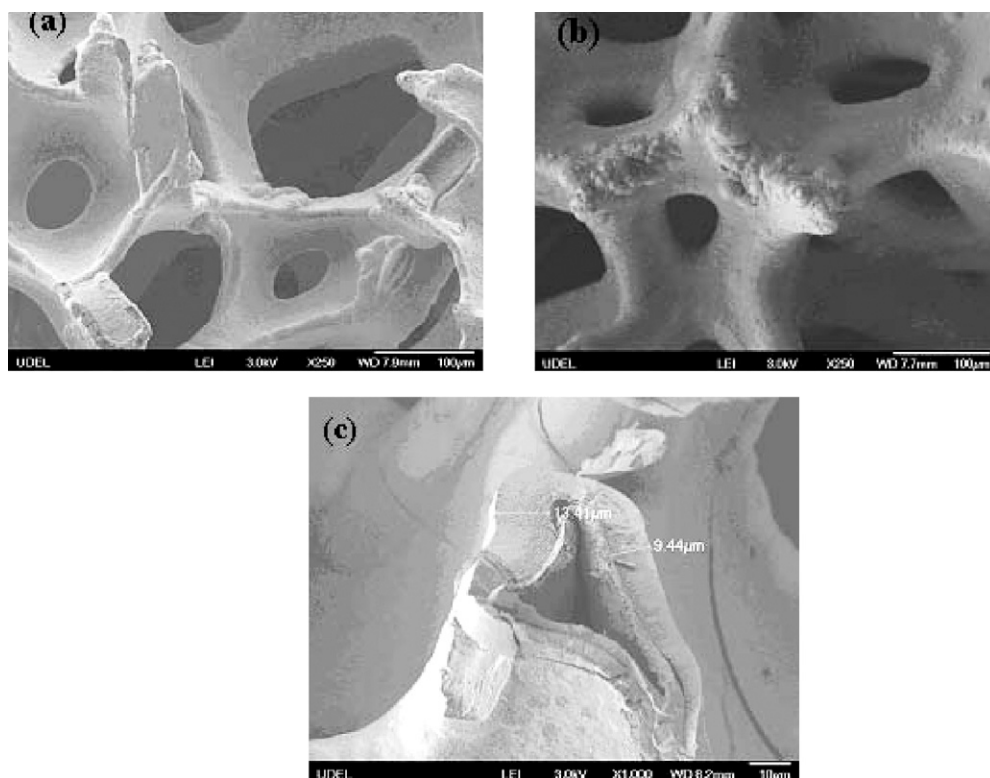


Fig. 3. SEM pictures: (a) Ni-foam template; (b) surface of electroless plated CoB/Ni-foam template; (c) cross-section of electroless plated CoB/Ni-foam template.

Table 3

Bath composition and plating conditions for electroplating of CoB thin-film alloy on Ni-foam templates

Experimental condition	Composition
CoSO ₄ ·7H ₂ O (M)	0.100–0.500
CoCl ₂ ·6H ₂ O (M)	0.100–0.500
H ₃ BO ₃ (M)	0.100–1.000
Current density (mAcm ⁻²)	80–320
pH	4–5
Temperature (°C)	60

NaBH₄ solution. The rate decreased on increasing the NaBH₄ concentration; similar observations have also been reported by previous researchers [7,8]. A H₂ generation rate of around 0.5 L min⁻¹ g⁻¹ was obtained with 20 wt.% NaBH₄ solution. At NaBH₄ concentrations beyond 25 wt.%, the solution becomes highly viscous due to the solidification of hydrolyzed metaborate. The generation of H₂ gas in the highly viscous solution leads to disintegration of the Ni-foam template. However, disintegration of the Ni-foam template could be avoided by periodic addition of water to the H₂ generator if concentrated NaBH₄ solutions (>25 wt.%) are used for H₂ generation.

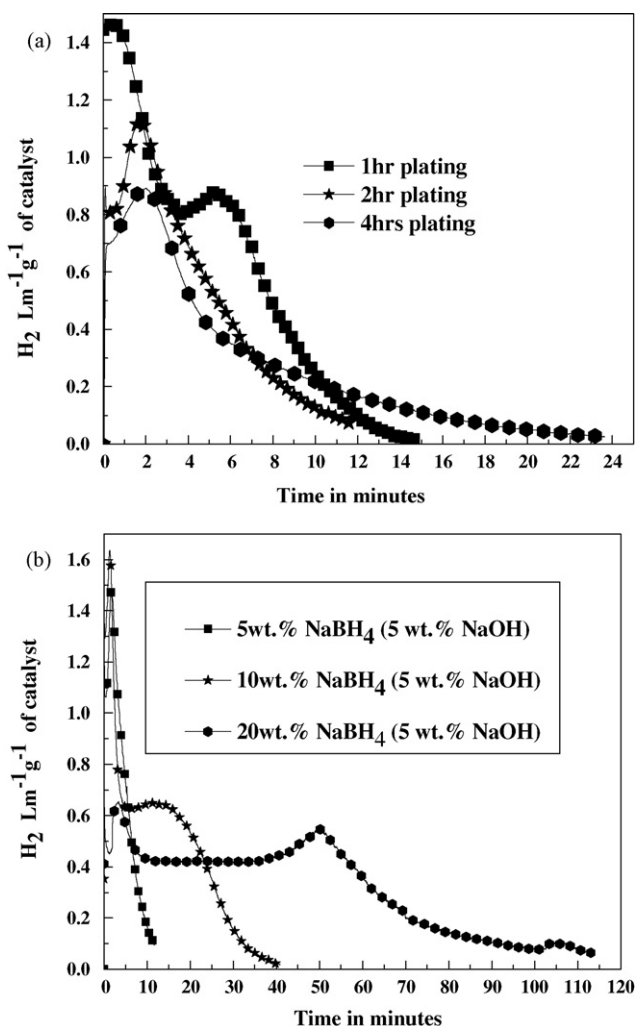


Fig. 4. H₂ generation using electroless plated CoB/Ni-foam templates. (a) Effect of electroless plating time, 5 wt.% NaBH₄ (5 wt.% NaOH); (b) effect of NaBH₄ concentration.

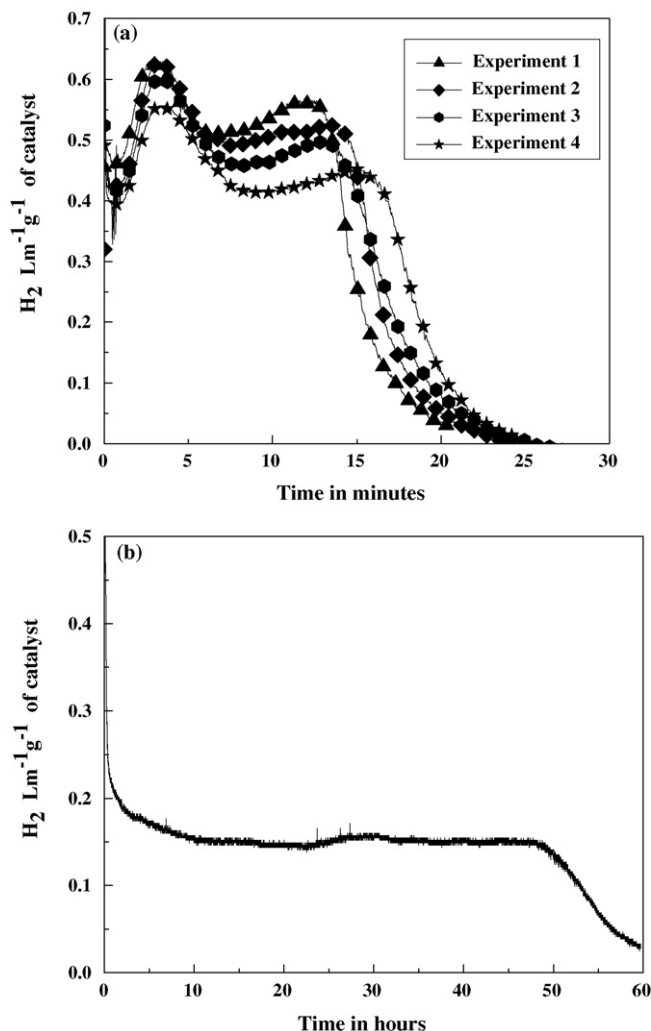


Fig. 5. H₂ generation using electroless plated CoB/Ni-foam template. (a) Repetitive use test, 5 wt.% NaBH₄ (5 wt.% NaOH); (b) extended durability test 10 wt.% NaBH₄ (5 wt.% NaOH).

The H₂ generation profiles plotted in Figs. 4 and 5 are not steady even while maintaining a constant temperature of the H₂ generation reactor. Once the catalyst coated Ni-foam template is immersed in NaBH₄ solution, H₂ generation commences immediately, the rate increases rapidly and reaches a maximum value, and then starts to decline and eventually reaches a more or less steady value (Fig. 5(a)). Chemical degradation of the CoB catalyst, reduction in catalyst surface area due to the adsorption of hydrolyzed metaborate or a combination of both could explain the unsteady H₂ generation profile. Kiessling [22] has reported that the stability of transition metal borides depends on the B content in the deposit and the stability increases with B content. However, further investigations are needed to identify the reasons for the unsteady H₂ generation profile of these catalysts.

As outlined in the introduction section, the thin-film catalyst templates are suitable for repetitive use. Once all the NaBH₄ is hydrolyzed, the spent metaborate could be drained and new NaBH₄ solution added to resume H₂ generation, or the template could be removed and re-used for the next experiment. In order to study this possibility, the same template was used in four subsequent experiments and the H₂ generation profiles are shown in Fig. 5(a). The rate of H₂ generation decreased slightly in subsequent experiments which could be due to the chemical

changes in the catalyst as discussed earlier. Although there is a gradual reduction of catalytic activity, the catalysts maintain their activity for prolonged durations. The template was washed, dried and weighed at the end of the four experiments to evaluate the loss of catalyst from the template; the loss was insignificant confirming the excellent adherence of the coating to the substrate.

Suitability for extended operation needs to be assessed for the commercial application of these catalyst templates. The electroless plated CoB/Ni-foam template was tested in 10 wt.% NaBH₄ (5 wt.% NaOH) for extended duration of up to 60 h and the H₂ generation profile is given in Fig. 5(b). The H₂ generation rate decreased substantially within 5 h; thereafter, the rate remained more or less constant up to 60 h which establishes their suitability for prolonged operation. There was very little weight loss of about ~2.0 wt.% after 60 h of testing.

3.2. Electroplating

Although durable thin-film catalyst templates could be prepared by the electroless plating technique, electroless plating is not a green chemical process. It involves the use of acidic organic compounds such as complexing agents and borane amine complexes as reducing agents. Since these are hazardous compounds, the spent solution from the electroless plating bath needs to be carefully handled following elaborate waste treatment methods. Such waste treatment can be expensive and also lead to environmental concerns. On the other hand, electroplating is a green technique where “electrons” are employed as the reagents. The spent solution requires no treatment; in fact, precursor Co salts could be easily isolated by the evaporation of the spent solution. Due to these inherent advantages, we were interested in exploring the electroplating technique for this study.

Previous researchers have used H₃BO₃ along with DMB as the source of B in the electroplating method to prepare NiB [14]. Since DMB itself is a reducing agent, it is quite possible that electroless plating could also occur simultaneously along with electroplating. Moreover, waste treatment and disposal of DMB spent solution could be an issue. Hence, only H₃BO₃ was selected as the source of B in this study. The electroplating bath composition and plating conditions are given in Table 3. The surface morphology of the CoB alloy deposit obtained with electroplating technique is shown in Fig. 6. Two distinct morphologies, i.e. agglomerate and rod forms can be observed in the deposits. Since the deposit is a mixture of CoB and

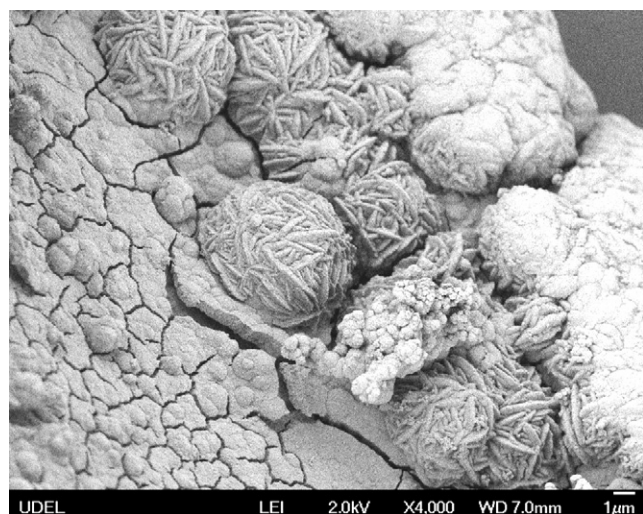


Fig. 6. SEM picture of the surface of electroplated CoB/Ni-foam template. Two distinct morphologies: agglomerate and rod forms can be observed.

Co metal, the two different morphologies could be due to the simultaneous presence of CoB and Co metal in the deposit. The B content in the deposits was in the range of 0.20–0.60 wt.% which is less than that of electroless plated samples. The B content in the deposit depends on the concentration of H₃BO₃ in the bath; B content increased from 0.20 to 0.60 wt.% when the H₃BO₃ concentration was increased from 0.100 to 0.75 M. The bath was not stable at higher concentrations due to the precipitation of H₃BO₃. Since a stainless steel strip was used as anode, the electroplated alloy deposits also contained about 5–10 wt.% of iron.

H₂ generation profiles of electroplated thin-film Co-B/Ni-foam templates are shown in Fig. 7. The H₂ generation profiles of templates prepared at different current densities are plotted in Fig. 7(i). H₂ generation rate is lowest when the template was prepared at a current density of 80 mA cm⁻²; at this current density, the voltage is not sufficient for ionization of borate and its incorporation in the deposit. H₂ generation was more or less the same with the templates prepared at higher current densities. The effect of H₃BO₃ concentration in the plating bath on H₂ generation efficiency is shown in Fig. 7(ii). The H₂ generation rate of the templates increases with increase in H₃BO₃ content in the plating bath up to 0.75 M; the H₂ generation rate of the template prepared

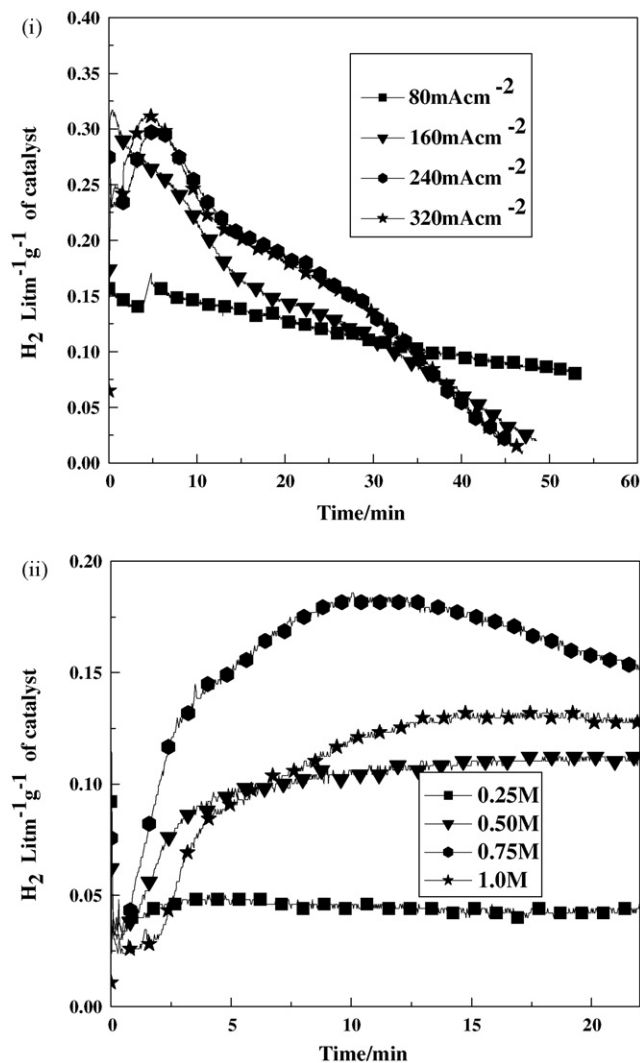


Fig. 7. H₂ generation using electroplated CoB/Ni-foam templates: (a) templates prepared at different current densities, 5 wt.% NaBH₄ (5 wt.% NaOH); (b) effect of boric acid (H₃BO₃) concentration, current density of template preparation, 80 mA cm⁻², 5 wt.% NaBH₄ (5 wt.% NaOH).

with 1.00 M H_3BO_3 is lower due to the unstable nature of the bath. Hence, 0.75 M H_3BO_3 could be considered as the optimum concentration for the deposition process.

3.3. Calculation of activation energy of the catalysts

H_2 generation increases linearly with temperature and drops suddenly after all of the NaBH_4 is hydrolyzed. Assuming zeroth-order kinetics for Co_2B -catalyzed H_2 generation as reported by earlier workers [10], the rate equation could be written as

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \quad (1)$$

where k is the reaction rate ($\text{mol min}^{-1} \text{g}^{-1}$), k_0 is the constant ($\text{mol min}^{-1} \text{g}^{-1}$), E is the activation energy, R is the universal gas constant, and T is the reaction temperature in Kelvin. In k was plotted against $1/T$ for H_2 generation by electroless plated as well as electroplated CoB/Ni -foam templates (Fig. 8). The activation energy from the slope was found to be 44.47 and 54.89 kJ mol^{-1} for the CoB/Ni -foam templates prepared using electroless and electroplating methods, respectively. The activation energy values are close to the value of 45.64 kJ mol^{-1} reported for the Co

activated carbon supported catalyst [23]. The difference in the activation energy of the electroless, electroplated catalysts is due to the difference in their composition. The normalized B content in the electroless plated catalyst template was in the range of 1.0–1.30 wt.%; where as, it was only 0.20–0.60 wt.% for the catalyst obtained by electroplating. This shows that the catalyst obtained by electroless plating will have more of CoB than that obtained by the electroplating method. Since CoB alloy is the active catalyst, lesser percentage of CoB alloy in the electroplated catalyst is the reason for higher activation energy of this catalyst when compared with that obtained with electroless plating method. The nickel foam template used in this work had density in the range of 300–600 g m^{-3} . Since the density will be reduced on coating the foam with the catalyst, we considered an approximate density of 300 g m^{-3} to calculate the volumetric productivity of the catalyst templates. From the H_2 generation rates plotted in Figs. 4, 5 and 7, a volumetric productivity in the range of 0.48–1.12 and 0.24 $\text{mol L}^{-1} \text{h}^{-1}$ was calculated for the electroless, electroplated CoB/Ni -foam catalyst templates, respectively.

Regarding the mechanism of action of CoB catalysts, Holbrook and Twist [24] have postulated the formation of transition metal hydride (M-H) as the initial step where M denotes the transition metal. In the transition metal borides, the higher electronegativity of B may polarize the M-B bond making the M highly electropositive. The positively charged transition metal (M) may act as efficient catalyst for the removal of H^- from NaBH_4 . Thus, excellent catalytic activity of CoB might be due to the polarization of Co-B bond due the higher electronegativity of B .

4. Conclusions

Highly adherent, durable, thin-film CoB alloy/ Ni -foam templates were prepared using electroless as well as electroplating techniques. The boron content in the deposits was less than that required for stoichiometric alloy formation. The thin-film catalyst templates were found to be suitable for repetitive use, though H_2 generation decreased slightly during subsequent experiments. Extended operation of the catalyst was explored up to 60 h thereby establishing the possibility of their commercial application. Use of these templates in commercial H_2 generators will simplify the design and reduce the fabrication cost.

Although thin-film CoB catalysts appear promising as cost-effective replacements for noble metal based catalysts for H_2 generation from NaBH_4 , further detailed investigations are necessary to understand the unsteady H_2 generation profile of these catalysts. This along with the identification of suitable bath conditions to improve boron content in the deposit will dramatically improve their commercial potential.

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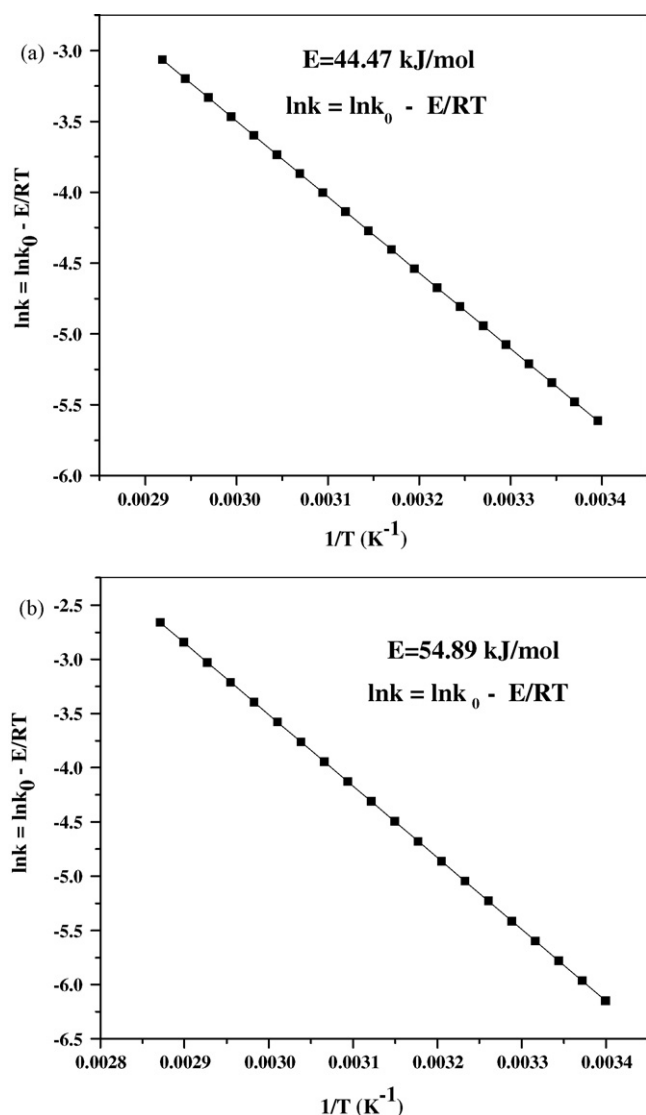


Fig. 8. $\ln k$ vs. $1/T$ plots. (a) Electroless plated Co-B/Ni -foam template; (b) electroplated CoB/Ni -foam template.

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